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PATENT ABSTRACTS OF JAPAN

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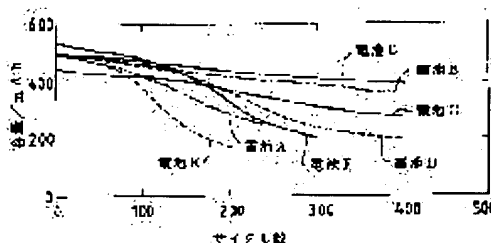
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(54) NONAQUEOUS ELECTROLYTE SECONDARY BATTERY GRAPHITE ELECTRODE AND NONAQUEOUS ELECTROLYTE SECONDARY BATTERY USING IT

(57)Abstract:

PURPOSE: To provide a nonaqueous electrolyte secondary battery, having high voltage, a high energy density, and excellent various battery characteristics with a cycle characteristic as a center, by improving the binder of a negative electrode.

CONSTITUTION: This graphite electrode is provided by applying a graphite mixture, in which the mixed dispersant of non-fluorine organic copolymer and fluorine organic copolymer having the subject of butadiene is added as a binder to graphite powder to be made a paste state, to both the surfaces of copper foil to be dried. The solid component in the mixed dispersant is made have a range of 3-7% by weight ratio to the graphite powder.



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CLAIMS

[Claim(s)]

[Claim 1] the graphite which added the mixed dispersant of a non-fluorine system organic polymer and a fluorine system organic polymer which made the butadiene the subject as a binder to the graphite powder, and was made into the shape of a paste -- the graphite electrode for nonaqueous electrolyte rechargeable batteries to which it is obtained by plastering both sides of copper foil with a mixture, and drying, and the formed element in the aforementioned mixed dispersant is characterized by being 3% - 7% in a weight ratio to the aforementioned graphite powder

[Claim 2] The graphite electrode for nonaqueous electrolyte rechargeable batteries according to claim 1 whose spacing (d002) of the 002nd page according [the above-mentioned graphite powder] to a wide angle X-ray diffraction method is 3.36Å - 3.40Å.

[Claim 3] The graphite electrode for nonaqueous electrolyte rechargeable batteries according to claim 1 or 2 which is at least one chosen from the group which the above-mentioned non-fluorine system organic polymer becomes from styrene / butadiene copolymer, acrylonitrile / butadiene copolymer, and a butadiene copolymer.

[Claim 4] The graphite electrode for nonaqueous electrolyte rechargeable batteries given in the claim 1 or any of 3 they are. which is at least one chosen from the group which the above-mentioned fluorine system organic polymer becomes from a tetrafluoroethylene polymer and a tetrafluoroethylene 6 fluoride / propylene / copolymer]

[Claim 5] The graphite electrode for nonaqueous electrolyte rechargeable batteries given in the claim 1 or any of 4 they are. whose rate for which the fluorine system organic polymer in the above-mentioned binder accounts is 20% - 50% in a weight ratio as a ratio of the solid content]

[Claim 6] The nonaqueous electrolyte rechargeable battery equipped with the negative electrode which consists of a graphite electrode for nonaqueous electrolyte rechargeable batteries given in any [the above-mentioned claim 1 or] of 5 they are, nonaqueous electrolyte, and the positive electrode which consists of a lithium content oxide.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to improvement of the negative electrode of small and a lightweight and new nonaqueous electrolyte rechargeable battery in more detail about the nonaqueous electrolyte rechargeable battery which used the graphite electrode for nonaqueous electrolyte rechargeable batteries, and this.

[0002]

[Description of the Prior Art] In recent years, portable-izing of consumer electronics and cordless-ization are progressing quickly. Small [which bears the power supply for a drive along with this], and the requests to the rechargeable battery which is lightweight and has high-energy density are also mounting. From such a viewpoint, as a cell by which a non-drainage system rechargeable battery, especially a lithium secondary battery especially have a high voltage and high-energy density, the expectation is great and development is hurried.

[0003] Conventionally, manganese dioxide, a vanadium pentoxide, 2 titanium sulfides, etc. were used for the positive active material of a lithium secondary battery. The cell was constituted from these positive electrodes, and a lithium negative electrode and the organic electrolytic solution, and charge and discharge were repeated. However, in the rechargeable battery which generally used the lithium metal for the negative electrode, a technical problem called the side reaction of the internal short circuit and active material by the dendrite-like lithium generated at the time of charge, and the electrolytic solution has been a serious obstacle to rechargeable-battery-izing. Furthermore, what is satisfied also in a high charge-and-discharge property or an overdischarge property is not found out.

[0004] Moreover, the safety of a lithium cell is pointed out severely and a very difficult state has reservation of safety these days in the fuel cell subsystem which used the lithium metal or the lithium alloy for the negative electrode.

[0005] The electrode active material using the intercalation reaction of a stratified compound new type recently attracts attention, and the intercalation compound is considered as an electrode material of a rechargeable battery. Especially the carbon material that can intercalate / deintercalate Li ion is promising as a negative-electrode material of a lithium secondary battery, and the development is performed briskly.

[0006] It is LiCoO₂ which is the compound which has a high voltage more as a positive active material in connection with using a carbon material for a negative electrode on the other hand, and contains Li. Using LiNiO₂ and the multiple oxide which replaced some of these Co(es) and nickel by other elements further is proposed. However, although high-energy density is obtained in this non-drainage system cell, it is difficult to obtain high power density compared with a drainage system cell. This has a large place resulting from the degree of ionic conduction of the electrolytic solution, and the present condition is that the degree of ionic conduction is 1/100 or less compared with solution in nonaqueous electrolyte.

[0007] It is possible to enlarge electrode area as a method for solving these troubles, namely, to use the plate of a large area in a thin form. The manufacturing method of applying the paste which made the solution distributing an electrode active material, and especially drying to the metallic foil which is a charge collector is known well, and it is possible to obtain the plate of a thin form and a large area comparatively easily.

[0008]

[Problem(s) to be Solved by the Invention] In the above electrode manufacturing methods, although it is easy to obtain the plate of a thin form and a large area when a negative-electrode board is manufactured by the technique of applying and drying the paste which made the solution distribute a graphite powder to both sides of the copper foil which is a charge collector, the influence which it has on the negative-electrode graphite material and charge collector of the binder is very large. the case where fluorine system organic polymers, such as Teflon generally well used as a binder, are used -- a mixture -- although the binding capacity of a between is powerful, the binding intensity of a mixture and the copper foil which is a charge collector becomes it is weak and lacking in current collection nature And when a cell is constituted, in charge and discharge, the satisfying result is not obtained in the cycle property or the elevated-temperature preservation property.

[0009] although it is possible for the binding property with copper foil to be good, and to obtain a plate easily in this case on the other hand, although using the binder of a non-fluorine system, for example, styrene / butadiene copolymer etc., is indicated by JP,4-51459,A -- a mixture -- expansion of the negative-electrode graphite material accompanying [the binding capacity of a between is weak compared with a fluorine system binder, and] charge and discharge, and contraction -- following -- a mixture -- strong degradation cannot be caused and neither a cycle property nor an elevated-temperature preservation property can be

[0010] moreover, the mixture by the expansion and contraction of a negative-electrode graphite accompanying charge and

discharge -- a strong fall has a close relation to the degree of the graphitization of the graphite to be used. When the carbon material of comparatively low crystallinity is used, a graphite layer structure is underdeveloped, and since the spacing is large, most expansion between the layers accompanying insertion of a lithium is not seen. therefore, the mixture accompanying charge and discharge -- a strong fall can obtain the negative-electrode board made into the purpose by using the above non-fluorine system binders very few. However, in such carbon material of low crystallinity, there are few amounts of the lithium which can be intercalated from a layer structure being underdeveloped, and only the capacity which is about 100-150 mAh/g can be obtained. Moreover, since the potential of the negative electrode at the time of electric discharge turns into electropositive potential, it becomes difficult for a cell voltage to become low and to obtain the cell of high capacity and high-energy density. Then, this invention persons decided to use the graphite material from which the graphite layer structure developed more for a negative electrode, as a result of observing the physical properties of negative-electrode carbon material aiming at high-capacity-izing more. although the increase in the amount of lithiums which can carry out an intercalation was attained and high capacity and high-energy density-ization were attained, in order [consequently,] to cause the expansion and contraction of a graphite accompanying the above charges and discharges by one side -- a mixture -- a result which a strong fall comes to be seen and mainly leaves a technical problem to a cycle property was brought

[0011]

[Means for Solving the Problem] the graphite which the graphite electrode for nonaqueous electrolyte rechargeable batteries of this invention added the mixed dispersant of a non-fluorine system organic polymer and a fluorine system organic polymer which made the butadiene the subject as a binder to the graphite powder, and was made into the shape of a paste in order to solve these technical problems -- it is obtained by plastering both sides of copper foil with a mixture, and drying, and the formed element in the aforementioned mixed dispersant is characterized by to be 3% - 7% in a weight ratio to the aforementioned graphite powder.

[0012] Although not limited especially as the above-mentioned graphite material, an artificial graphite, a natural graphite, etc. of a thing or marketing which heat-treated carbon fibers, such as the carbon material of graphitizability, for example, corks, mesophase carbon, a pyrolytic carbon, and a mesophase pitch based carbon fiber, a vapor-growth system carbon fiber, at the elevated temperature of 2000 degrees C or more, and graphitized them can be used. The mean particle diameter has a 1-20-micrometer desirable thing, and a carbon fiber can be similarly plate-ized by grinding.

[0013] As for the above-mentioned graphite powder, it is desirable that the spacing (d002) of the 002nd page by the wide angle X-ray diffraction method is 3.36Å - 3.40Å.

[0014] Moreover, as for the above-mentioned non-fluorine system organic polymer, it is desirable that it is at least one chosen from the group which consists of styrene / butadiene copolymer, acrylonitrile / butadiene copolymer, and a butadiene copolymer.

[0015] Moreover, as for the above-mentioned fluorine system organic polymer, it is desirable that it is at least one chosen from the group which consists of a tetrafluoroethylene polymer and a tetrafluoroethylene 6 fluoride [propylene] copolymer.

[0016] Moreover, as for the rate for which the fluorine system organic polymer in the above-mentioned binder accounts, it is desirable that it is 20% - 50% in a weight ratio as a ratio of the solid content.

[0017] less than 20% -- a graphite -- a mixture -- 200 cycle was exceeded, although sufficient effect was not acquired in the binding property of a between but it was satisfactory in early stages of the cycle -- it hits and capacity degradation of a shell becomes remarkable. Conversely, a result to which current collection nature with copper foil becomes inadequate when 50% is exceeded, especially a capacity maintenance factor becomes low in the elevated-temperature shelf life in a charge state is brought.

[0018] Moreover, it is [plate-izing] easier to be a manufacturing process waterworks solution, although the binder to add is not cared about even if it is desirable to use a fluorine system and a non-fluorine system in the state where the solution was made to distribute the powder of a particle, it is solution as a dispersant, and it is a non-aqueous solvent.

[0019] moreover, a graphite -- a mixture -- pasting -- facing -- for example, thickeners, such as a carboxymethyl cellulose, -- some -- ***** -- things are also made

[0020] Moreover, it is characterized by equipping the nonaqueous electrolyte rechargeable battery of this invention with the negative electrode which consists of the aforementioned ***** for nonaqueous electrolyte rechargeable batteries, nonaqueous electrolyte, and the positive electrode which consists of a lithium content oxide.

[0021] It can be said that it is suitable since propylene carbonate (it omits Following PC) is hardly accompanied by side reaction like [since a decomposition reaction is started and there is an inclination accompanied by the generation of gas at the time of charge / in case the ethylene carbonate (it omits Following EC) which is the same annular carbonate preferably is PC] when graphite material is used for a negative electrode, although the thing better known than before as the above-mentioned electrolytic solution could be used. However, since EC is very a high-melting point and a solid-state in ordinary temperature, use with an independent solvent is difficult. Therefore, it is desirable to use 1 and 2-dimethoxyethane which is the low melting point and is the solvent of low viscosity, diethyl carbonate (for it to omit Following DEC), and the mixed solvent which mixed aliphatic carboxylates, such as a methyl propionate (it omits Following MP), further. Moreover, each what are better known than the former, such as a 6 fluoride [phosphoric-acid] lithium, hoe lithium fluoride, a 6 fluoride [arsenic acid] lithium, and a lithium perchlorate, as a salt of Li which dissolves in these solvents can use it.

[0022] LiCoO₂ which is the compound which contains a lithium ion in a positive electrode on the other hand, LiNiO₂, LiFeO₂, and LiMn₂O₄ etc. -- it is usable. The above-mentioned multiple oxide can be easily obtained by mixing and calcinating these according to the purpose composition by using the carbonate or oxide of a lithium or cobalt as a raw material. When other raw materials are used, of course, it can compound similarly. It is LiCoO₂ especially. Charge-and-discharge possible capacity is the

largest, and chemically stable in the above-mentioned electrolytic solution. Usually, the burning temperature is set up among 650 degrees C - 1200 degrees C.

[0023]

[Function] a graphite above paste type -- adding the mixed dispersant of a non-fluorine system organic polymer and a fluorine system organic polymer which made the butadiene the subject as the binder, when obtaining the graphite electrode of a large area in a thin form with a mixture -- both feature -- employing efficiently -- a mixture -- while maintaining the binding capacity of a between, current collection nature with the copper foil which is a charge collector also becomes possible [obtaining a good and firm plate]

[0024] However, the ratio of the binder to add is promotion to a responsible post, and it is required for the formed element in a mixed dispersant to be 3% - 7% in a weight ratio to a graphite powder. less than 3% -- a mixture -- the binding property of a between becomes inadequate and capacity degradation becomes remarkable in a cycle property, especially a rapid charge-and-discharge property the case where 7% is exceeded on the other hand -- a graphite -- the pack density of a mixture falls, the charge-and-discharge depth of a negative electrode becomes large, and a cycle property is affected Moreover, decline in the conductivity of a plate is seen, the internal resistance of a cell increases, and a result in which the charge-and-discharge property of a high rate is inferior is brought.

[0025]

[Example] Hereafter, an example describes this invention in detail.

(Example 1) Drawing of longitudinal section of the cylindrical shape cell used for drawing 1 by this example is shown. In drawing, the cell case into which 1 processed the stainless steel plate of organic-proof electrolytic-solution nature, the obturation board with which 2 prepared the relief valve, and 3 show insulating packing. 4 is a group of electrode, and a positive electrode and a negative electrode are wound in the shape of a multiple-times swirl through separator, and it is contained in the case 1. And from the above-mentioned positive electrode, the positive-electrode lead 5 is pulled out and it connects with the obturation board 2, and from the negative electrode, the negative-electrode lead 6 is pulled out and it connects with the pars basilaris ossis occipitalis of the cell case 1. 7 is prepared in the vertical section of a group of electrode 4 with the insulating ring, respectively. Hereafter, positive, a negative-electrode board, etc. are explained in detail.

[0026] A positive electrode is Li_2Co_3 . Co_3O_4 LiCoO_2 which was mixed, calcinated for 10 hours and was compounded at 900 degrees C 7 weight sections mixture of the acetylene black 3 weight section and the polytetrafluoroethylene dispersion (by Daikin Industries, LTD. D-1, 60 % of the weight of solid contents) was carried out by the solid-content ratio, and carboxymethyl-cellulose solution was made to suspend in the powder 100 weight section, and it was made the shape of a paste at it. Both sides of aluminum foil with a thickness of 0.03mm were plastered with this paste, and it rolled out after dryness, and considered as the plate with the thickness of 0.17mm, a width of face [of 40mm], and a length of 250mm.

[0027] To a negative electrode, the mesophase microsphere generated in the carbonization process of a pitch the material (d002=3.37Å) 100 weight section which heat-treated and graphitized the meso carbon micro bead (it omits Following MCMB) used as the raw material at 2800 degrees C --styrene / butadiene rubber dispersion (SBR by Japan Synthetic Rubber Co., Ltd. --) the mixing ratio which shows 48 % of the weight of solid contents, and a polytetrafluoroethylene dispersion (by Daikin Industries, LTD. D-1, 60 % of the weight of solid contents) in Table 1 -- mixed at the rate, carboxymethyl-cellulose solution was made to suspend, and it was made the shape of a paste And both sides of copper foil with a thickness of 0.02mm were plastered with this paste, and it rolled out after dryness, and considered as the plate with the thickness of 0.20mm, a width of face [of 42mm], and a length of 270mm.

[0028] And the lead was attached in positive and each negative-electrode board, and the cell case with winding, a diameter [of 14.0mm], and a height of 50mm was spirally supplied through the separator made from polyethylene with the thickness of 0.025mm, a width of face [of 46mm], and a length of 730mm. It is one mol [l.] LiPF_6 to the solvent which mixed MP with EC by the volume ratio of DEC and 20:40:40 to the electrolytic solution. Using what was dissolved, after pouring this in, it obturated, and it considered as the examination cell.

[0029] Evaluation of an examination cell performed constant-potential charge made into charge voltage 4.1V, and charging-time 1 hour, and limit current was set to 600mA. Electric discharge performed 500mA of discharge currents, and constant-current discharge of discharge-final-voltage 3.0V, and performed the cycle examination under 20-degree C environment. Comparison of the cycle property is shown in drawing 2 .

[0030]

[Table 1]

電池	S B R (固形分重量%)	ポリ四フッ化エチレン 樹脂 (固形分重量%)
電池 A	5	0
電池 B	3	3
電池 C	3	2
電池 D	2	3
電池 E	0	5
電池 F	1	1
電池 G	5	3

[0031] the cell E which used only the cell A which used only SBR, and the polytetrafluoroethylene resin from the result of the cycle property of drawing 2 -- both -- a property -- inadequate -- this -- each -- a mixture -- the binding capacity of a between, and a mixture -- it is thought that it is because the both sides of the binding capacity between /charge collectors cannot be satisfied. Therefore, it can be said that it is required to use the both sides of SBR and a polytetrafluoroethylene resin as a binder. However, in Cell F, since there are few total amounts of binders, binding capacity becomes inadequate and a cycle property cannot be satisfied. Conversely, by Cell G, since there were too many total binders, polarization of a negative electrode became large, and a result to which cell capacity falls was brought. Although both Cell B, the cell C, and the cell D have high capacity and the comparatively good cycle property was able to be given, a difference comes to be looked at by the cycle property above about 200 cycles, and the ratio of the polytetrafluoroethylene resin in a binder can say that the property in the second half of a cycle has 50% or less and the fewer good one. Therefore, the ratio of both binder can also be referred to as being an important factor.

(Example 2) The petroleum coke from which the heat treatment temperature shown in Table 2 differs was chosen as the carbon material of a negative electrode, polytetrafluoroethylene / 6 fluoride [propylene] dispersion (1 50 % of the weight of solid contents [ND/ by Daikin Industries, LTD. /-]) was mixed for acrylonitrile / butadiene rubber dispersion (NBR by Japan Synthetic Rubber Co., Ltd., 40 % of the weight of solid contents) 2% of the weight 3% of the weight as a binder, respectively, except it, the cell was constituted completely like the example 1 and the same charge and discharge test was performed. Comparison of the discharge curve of each 10 cycle eye was shown in drawing 3.

[0032]

[Table 2]

電池	熱処理温度	d 0 0 2 / Å
電池 H	1 0 0 0 °C	3 . 5 0
電池 I	1 8 0 0 °C	3 . 4 2
電池 J	2 2 0 0 °C	3 . 4 0
電池 K	2 8 0 0 °C	3 . 3 6

[0033] By the cells H and I using the low petroleum coke of heat treatment temperature, service capacity is small and drawing 3 shows a bird clapper. It is thought that it is because the amount of lithiums which graphitization does not fully progress in these temperature fields, but can intercalate this from a layer structure being underdeveloped is restricted. Moreover, it can be said that the inclination of discharge voltage is especially large by Cell H, and it is in the inclination for average voltage to become low. This is also dependent on the degree of the graphitization of a negative electrode. Therefore, in order to obtain the cell of high capacity and the high voltage more, in other words, the degree of graphitization is very important, and it is desirable the heat treatment temperature of negative-electrode graphite material and that the spacing (d002) of the 002nd page is 3.40Å or less.

[0034] In addition, at this examples 1 and 2, it is LiCoO₂ to a positive electrode. Although used, when other above-mentioned lithium content oxides were used, although the difference of some capacity was seen, the almost same effect was acquired.

[0035]

[Effect of the Invention] It has high capacity and high-energy density, and it is effective in the ability to be able to offer the nonaqueous-electrolyte rechargeable battery excellent also in the cycle property by adding the mixed dispersant of a non-fluorine

system organic polymer and a fluorine system organic polymer which made the butadiene the subject as a binder to a graphite powder, and using the electrode of the application formula which the formed element made 3% - 7% by the weight ratio to the graphite powder for a negative electrode so that clearly from the above explanation.

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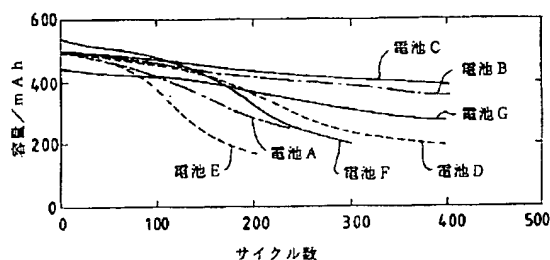
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(54)【発明の名称】 非水電解液二次電池用黒鉛電極およびこれを用いた非水電解液二次電池

(57)【要約】

【目的】 負極のバインダーの改良によって高電圧、高エネルギー密度を有し、サイクル特性を中心とする電池諸特性に優れた非水電解液二次電池を提供する。

【構成】 黒鉛粉末にバインダーとしてブタジエンを主体とした非フッ素系有機重合体とフッ素系有機重合体の混合分散剤を加え、ペースト状にした黒鉛合剤を銅箔の両面に塗着、乾燥することによって得られたものであって、前記混合分散剤中の固形成分が前記黒鉛粉末に対して重量比で3%~7%の範囲とする。



1

【特許請求の範囲】

【請求項1】 黒鉛粉末にバインダーとしてブタジエンを主体とした非フッ素系有機重合体とフッ素系有機重合体の混合分散剤を加え、ペースト状にした黒鉛合剤を銅箔の両面に塗着、乾燥することによって得られたものであって、前記混合分散剤中の固形成分が前記黒鉛粉末に対して重量比で3%~7%であることを特徴とする非水電解液二次電池用黒鉛電極。

【請求項2】 上記黒鉛粉末が、広角X線回折法による002面の面間隔(d002)が3.36Å~3.40Åである請求項1記載の非水電解液二次電池用黒鉛電極。

【請求項3】 上記非フッ素系有機重合体が、スチレン/ブタジエン共重合体、アクリロニトリル/ブタジエン共重合体、ブタジエン共重合体からなる群から選ばれた少なくとも1つである請求項1または2記載の非水電解液二次電池用黒鉛電極。

【請求項4】 上記フッ素系有機重合体が、四フッ化エチレン重合体、四フッ化エチレン六フッ化プロピレン共重合体からなる群から選ばれた少なくとも1つである請求項1乃至3の何れかに記載の非水電解液二次電池用黒鉛電極。

【請求項5】 上記バインダー中のフッ素系有機重合体の占める割合が、その固形分の比率として重量比で20%~50%である請求項1乃至4の何れかに記載の非水電解液二次電池用黒鉛電極。

【請求項6】 上記請求項1乃至5の何れかに記載の非水電解液二次電池用黒鉛電極からなる負極と、非水電解液と、リチウム含有酸化物からなる正極とを備えた非水電解液二次電池。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、非水電解液二次電池用黒鉛電極およびこれを用いた非水電解液二次電池に関し、さらに詳しくは小形、軽量で新規な非水電解液二次電池の負極の改良に関する。

【0002】

【従来の技術】近年、民生用電子機器のポータブル化、コードレス化が急速に進んでいる。これにつれて駆動用電源を担う小形、軽量で、かつ高エネルギー密度を有する二次電池への要望も高まっている。このような観点から、非水系二次電池、特にリチウム二次電池は、とりわけ高電圧、高エネルギー密度を有する電池としてその期待は大きく、開発が急がれている。

【0003】従来、リチウム二次電池の正極活物質には、二酸化マンガ、五酸化バナジウム、二硫化チタンなどが用いられていた。これらの正極と、リチウム負極および有機電解液とで電池を構成し、充放電を繰り返していた。ところが、一般に負極にリチウム金属を用いた二次電池では、充電時に生成するデンドライト状リチウ

2

ムによる内部短絡や活物質と電解液の副反応といった課題が二次電池化への大きな障害となっている。更には、高率充放電特性や過放電特性においても満足するものが見出されていない。

【0004】また、昨今、リチウム電池の安全性が厳しく指摘されており、負極にリチウム金属あるいはリチウム合金を用いた電池系においては安全性の確保が非常に困難な状態にある。

【0005】最近になって、層状化合物のインターカレーション反応を利用した新しいタイプの電極活物質が注目を集めており、層間化合物が二次電池の電極材料として考えられている。特に、Liイオンをインターカレート/デインターカレートし得る炭素材料はリチウム二次電池の負極材料として有望であり、その開発が盛んに行なわれている。

【0006】一方、負極に炭素材料を用いることに伴い、正極活物質としてはより高電圧を有し、かつLiを含む化合物であるLiCoO₂やLiNiO₂、更にはこれらのCoおよびNiの一部を他元素で置換した複合酸化物を用いることが提案されている。しかしながら、かかる非水系電池においては高エネルギー密度が得られるものの、水系電池に比べ高出力密度を得ることは困難である。これは電解液のイオン電導度に起因するところが大きく、非水電解液では水溶液に比べそのイオン電導度は100分の1以下であるのが現状である。

【0007】これらの問題点を解決するための方法として電極面積を大きくする、即ち薄形で大面積の極板を用いることが考えられる。とりわけ、集電体である金属箔に電極活物質を溶液に分散させたペーストを塗着、乾燥するといった製造法がよく知られており、比較的容易に薄形、大面積の極板を得ることが可能である。

【0008】

【発明が解決しようとする課題】前述のような電極製造法において、黒鉛粉末を溶液に分散させたペーストを集電体である銅箔の両面に塗着、乾燥するといった手法により負極板を製造した場合、薄形、大面積の極板を得ることは容易であるが、そのバインダーの負極黒鉛材および集電体に与える影響が極めて大きい。バインダーとして一般によく用いられているテフロンなどのフッ素系有機重合体を用いた場合、合剤間の結着力は強力であるが、合剤と集電体である銅箔との結着強度が弱く集電性に乏しくなる。そして電池を構成した場合、充放電においてそのサイクル特性や高温保存特性において満足のいく結果が得られていない。

【0009】一方、非フッ素系のバインダー、例えばスチレン/ブタジエン共重合体などを用いることが特開平4-51459号に開示されているが、この場合、銅箔との結着性はよく、容易に極板を得ることが可能であるが、合剤間の結着力はフッ素系バインダーに比べると弱く、充放電に伴う負極黒鉛材の膨張、収縮に伴って合剤

強度の劣化を引き起こし、結果としてサイクル特性や高温保存特性を満足することができない。

【0010】また、充放電に伴う負極黒鉛の膨張および収縮による合剤強度の低下は、用いる黒鉛の黒鉛化の度合と密接な関係がある。比較的低結晶性の炭素材を用いた場合、黒鉛層構造が未発達でありその面間隔が大きいために、リチウムの挿入に伴う層間の膨張はほとんど見られない。従って、充放電に伴う合剤強度の低下は非常に少なく上述のような非フッ素系バインダーを使用することで目的とする負極板を得ることができる。しかしながら、このような低結晶性の炭素材では層構造が未発達であることからインターカレートし得るリチウムの量が少なく、100～150mAh/g程度の容量しか得ることができない。また放電時の負極の電位が貴な電位となるために電池電圧が低くなり高容量、高エネルギー密度の電池を得ることは困難となる。そこで本発明者らはより高容量化を目指し負極炭素材の物性に注目した結果、より黒鉛層構造の発達した黒鉛材料を負極に使用することにした。その結果、インターカレーションし得るリチウム量の増加を達成し高容量、高エネルギー密度化が可能となったが、一方で前述のような充放電に伴う黒鉛の膨張および収縮を引き起こすために合剤強度の低下が見られるようになり主にサイクル特性に課題を残す結果となった。

【0011】

【課題を解決するための手段】これらの課題を解決するために、本発明の非水電解液二次電池用黒鉛電極は黒鉛粉末にバインダーとしてブタジエンを主体とした非フッ素系有機重合体とフッ素系有機重合体の混合分散剤を加え、ペースト状にした黒鉛合剤を銅箔の両面に塗着、乾燥することによって得られたものであって、前記混合分散剤中の固形成分が前記黒鉛粉末に対して重量比で3%～7%であることを特徴とする。

【0012】上記黒鉛材料としては特に限定されるものではないが、易黒鉛化性の炭素材、例えばコークス類、メソフェーズカーボン、熱分解炭素やメソフェーズピッチ系炭素繊維、気相成長系炭素繊維などの炭素繊維を2000℃以上の高温で熱処理を施し、黒鉛化したものや市販の人造黒鉛や天然黒鉛などが使用できる。その平均粒径は1～20μmのものが好ましく、炭素繊維は粉碎することによって同様に極板化することができる。

【0013】上記黒鉛粉末は、広角X線回折法による002面の面間隔(d002)が3.36Å～3.40Åであることが好ましい。

【0014】また、上記非フッ素系有機重合体は、スチレン/ブタジエン共重合体、アクリロニトリル/ブタジエン共重合体、ブタジエン共重合体からなる群から選ばれた少なくとも1つであることが好ましい。

【0015】また、上記フッ素系有機重合体は、四フッ化エチレン重合体、四フッ化エチレン六フッ化プロピレ

ン共重合体からなる群から選ばれた少なくとも1つであることが好ましい。

【0016】また、上記バインダー中のフッ素系有機重合体の占める割合は、その固形分の比率として重量比で20%～50%であることが好ましい。

【0017】20%未満では黒鉛合剤間の結着性において十分な効果が得られず、サイクル初期では問題はないが、200サイクルを越えたあたりからの容量劣化が顕著となる。逆に50%を越えた場合は銅箔との集電性が不十分となり、特に充電状態での高温保存性において容量維持率が低くなる結果となる。

【0018】また、加えるバインダーは、フッ素系、非フッ素系共に微粒子の粉末を溶液に分散させた状態で使用することが好ましく、分散剤としては水溶液であっても非水溶媒であってもかまわないが、製造工程上水溶液である方が極板化が容易である。

【0019】また、黒鉛合剤をペースト化するに際して、例えばカルボキシメチルセルロースなどの増粘剤を若干量加えることもできる。

【0020】また、本発明の非水電解液二次電池は前記非水電解液二次電池用黒鉛電極からなる負極と、非水電解液と、リチウム含有酸化物からなる正極とを備えたことを特徴とする。

【0021】上記電解液としては従来より公知のものが使用できるが、黒鉛材料を負極に使用した場合、プロピレンカーボネート（以下PCと略す）は充電時に分解反応を起こしガス発生を伴う傾向があるために好ましくなく、同様な環状カーボネートであるエチレンカーボネート（以下ECと略す）がPCの場合のような副反応をほとんど伴わないために適していると言える。しかしながら、ECは非常に高融点であり常温では固体であるために単独溶媒での使用は困難である。従って、低融点で且つ低粘性の溶媒である1,2-ジメトキシエタンやジエチルカーボネート（以下DECと略す）、更にはプロピオン酸メチル（以下MPと略す）などの脂肪族カルボン酸エステルを混合した混合溶媒を用いることが好ましい。また、これらの溶媒に溶解するLiの塩としては六フッ化リン酸リチウム、ホウフッ化リチウム、六フッ化ヒ酸リチウム、過塩素酸リチウムなど従来より公知のものがいずれも使用できる。

【0022】一方、正極にはリチウムイオンを含む化合物であるLiCoO₂、LiNiO₂、LiFeO₂、LiMn₂O₄などが使用可能である。上記複合酸化物は、例えばリチウムやコバルトの炭酸塩あるいは酸化物を原料として、目的組成に応じてこれらを混合し焼成することによって容易に得ることができる。勿論他の原料を用いた場合においても同様に合成できる。中でもLiCoO₂が充放電可能容量が最も大きく、且つ上記電解液中において化学的に安定である。通常その焼成温度は650℃～1200℃の間に設定される。

【0023】

【作用】前述のようなペーストタイプの黒鉛合剤によって薄形で大面積の黒鉛電極を得る場合、そのバインダーとしてブタジエンを主体とした非フッ素系有機重合体とフッ素系有機重合体の混合分散剤を加えることによって、両者の特長を生かし、合剤間の結着力を保つと共に集電体である銅箔との集電性も良好で強固な極板を得ることが可能となる。

【0024】但し、加えるバインダーの比率が重用であり、混合分散剤中の固形成分が黒鉛粉末に対して重量比で3%~7%であることが必要である。3%未満では合剤間の結着性が不十分となり、サイクル特性、特に急速充放電特性において容量劣化が顕著となる。一方、7%を越えた場合は黒鉛合剤の充填密度が低下し、負極の充放電深度が大きくなりサイクル特性に影響を与える。また、極板の導電率の低下が見られ電池の内部抵抗が増加し、ハイレートの充放電特性が劣る結果となる。

【0025】

【実施例】以下、実施例により本発明を詳しく述べる。

(実施例1) 図1に本実施例で用いた円筒形電池の縦断面図を示す。図において、1は耐有機電解液性のステンレス鋼板を加工した電池ケース、2は安全弁を設けた封口板、3は絶縁パッキングを示す。4は極板群であり、正極および負極がセパレータを介して複数回渦巻状に巻回されてケース1内に収納されている。そして上記正極からは正極リード5が引き出されて封口板2に接続され、負極からは負極リード6が引き出されて電池ケース1の底部に接続されている。7は絶縁リングで極板群4の上下部にそれぞれ設けられている。以下、正、負極板等について詳しく説明する。

【0026】正極は Li_2CO_3 と CO_3O_4 とを混合し、900℃で10時間焼成して合成した LiCoO_2 の粉末100重量部に、アセチレンブラック3重量部、ポリ四フッ化エチレンジスパーション(ダイキン工業社製 D-1、固形分60重量%)を固形分比率で7重*

*量部混合し、カルボキシメチルセルロース水溶液に懸濁させてペースト状にした。このペーストを厚さ0.03mmのアルミ箔の両面に塗着し、乾燥後圧延して厚さ0.17mm、幅40mm、長さ250mmの極板とした。

【0027】負極にはピッチの炭素化過程で生成するメソフェーズ小球体を原料としたメソカーボンマイクロビーズ(以下MCMBと略す)を2800℃で熱処理を施し黒鉛化した材料(d002=3.37Å)100重量部にスチレン/ブタジエンゴムディスパーション(日本合成ゴム株式会社製 SBR、固形分48重量%)とポリ四フッ化エチレンジスパーション(ダイキン工業社製 D-1、固形分60重量%)とを表1に示す混合比率で混合し、カルボキシメチルセルロース水溶液に懸濁させてペースト状にした。そしてこのペーストを厚さ0.02mmの銅箔の両面に塗着し、乾燥後圧延して厚さ0.20mm、幅42mm、長さ270mmの極板とした。

【0028】そして正、負極板それぞれにリードを取り付け、厚さ0.025mm、幅46mm、長さ730mmのポリエチレン製セパレータを介して渦巻状に巻回し、直径14.0mm、高さ50mmの電池ケースに納入した。電解液にはECとDECとMPを20:40:40の体積比で混合した溶媒に1モル/リットルの LiPF_6 を溶解したものをを用い、これを注液した後封口し、試験電池とした。

【0029】試験電池の評価は充電電圧4.1V、充電時間1時間とした定電圧充電を行い、制限電流を600mAとした。放電は放電電流500mA、放電終止電圧3.0Vの定電流放電を行い、20℃の環境下でサイクル試験を行なった。そのサイクル特性の比較を図2に示す。

【0030】

【表1】

電池	SBR (固形分重量%)	ポリ四フッ化エチレン 樹脂(固形分重量%)
電池A	5	0
電池B	3	3
電池C	3	2
電池D	2	3
電池E	0	5
電池F	1	1
電池G	5	3

【0031】図2のサイクル特性の結果より、SBRのみを使用した電池Aおよびポリ四フッ化エチレン樹脂のみを使用した電池Eでは共に特性が不十分であり、これはそれぞれが合剤間の結着力と合剤／集電体間の結着力の双方を満足できていないことによるものと考えられる。したがって、結着剤としてはSBRとポリ四フッ化エチレン樹脂の双方を用いることが必要であると言える。しかしながら、電池Fにおいては総結着剤量が少ないために結着力が不十分となりサイクル特性を満足できない。逆に電池Gでは総結着剤が多すぎるために負極の分極が大きくなり、電池容量が低下する結果となった。電池B、電池Cおよび電池Dは共に高容量を有し比較的良好なサイクル特性を与えることができたが、約200サイクル以上でサイクル特性に差が見られるようになり、バインダー中のポリ四フッ化エチレン樹脂の比率が*

*50%以下と少ない方がサイクル後期の特性が良好であると言える。したがって、両者のバインダーの比率も重要な因子であると言える。

(実施例2) 負極の炭素材料に表2に示す熱処理温度の異なる石油コークスを選択し、それぞれバインダーとしてアクリロニトリル／ブタジエンゴムディスパーション(日本合成ゴム株式会社製 NBR、固形分40重量%)を3重量%、ポリ四フッ化エチレン／六フッ化プロピレンディスパーション(ダイキン工業社製 ND-1、固形分50重量%)を2重量%混合し、それ以外は実施例1と全く同様に電池を構成し同様な充放電試験を行なった。それぞれの10サイクル目の放電曲線の比較を図3に示した。

【0032】

【表2】

電池	熱処理温度	d002/Å
電池H	1000℃	3.50
電池I	1800℃	3.42
電池J	2200℃	3.40
電池K	2800℃	3.36

【0033】図3より、熱処理温度の低い石油コークスを用いた電池HおよびIでは放電容量が小さくなることわかる。これはこれらの温度領域では黒鉛化が充分に進んでおらず、層構造が未発達であることからインターカレートし得るリチウム量が制限されることによると考えられる。また、特に電池Hでは放電電圧の勾配が大きく、平均電圧が低くなる傾向にあると言える。これも負極の黒鉛化の度合いに依存する。したがって、より高容量、高電圧の電池を得るためには負極黒鉛材の熱処理温度、言い換えれば黒鉛化の度合いが非常に重要であり、002面の面間隔(d002)が3.40Å以下であることが好ましい。

【0034】なお、本実施例1および2では正極にLiC₆O₂を用いたが、上述の他のリチウム含有酸化物を用いた場合も若干の容量の差は見られるもののほぼ同様な効果が得られた。

【0035】

【発明の効果】以上の説明から明らかなように、黒鉛粉末にバインダーとしてブタジエンを主体とした非フッ素※

※系有機重合体とフッ素系有機重合体の混合分散剤を加え、その固形成分が黒鉛粉末に対して重量比で3%~7%とした塗着式の電極を負極に使用することによって、高容量、高エネルギー密度を有し、サイクル特性にも優れた非水電解液二次電池を提供することができるといった効果がある。

【図面の簡単な説明】

【図1】本発明の実施例における円筒形電池の縦断面図

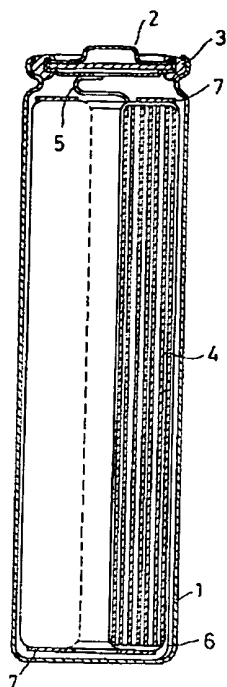
【図2】実施例1におけるサイクル特性の比較を示す図

【図3】実施例2における放電曲線の比較を示す図

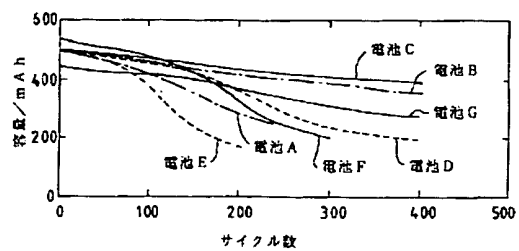
【符号の説明】

- 1 電池ケース
- 2 封口板
- 3 絶縁パッキング
- 4 極板群
- 5 正極リード
- 6 負極リード
- 7 絶縁リング

【図1】



【図2】



【図3】

